# Resist outgassing characterization of PAG-blended and PAG-bound systems

Kazuhiro Katayama, Toshiya Takahashi, Norihiko Sugie, Isamu Takagi
Yukiko Kikuchi, Eishi Shiobara, Hiroyuki Tanaka, Soichi Inoue
Takeo Watanabe*, Tetsuo Harada*, Hiroo Kinoshita*

EUVL Infrastructure Development Center, Inc. (EIDEC)
*Center for EUVL, University of Hyogo

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# Outline

- Introduction and Objective
- Experiment and results
  - PAG blend system: PAG cation size
  - PAG bound system: anion bound and cation bound
- Summary

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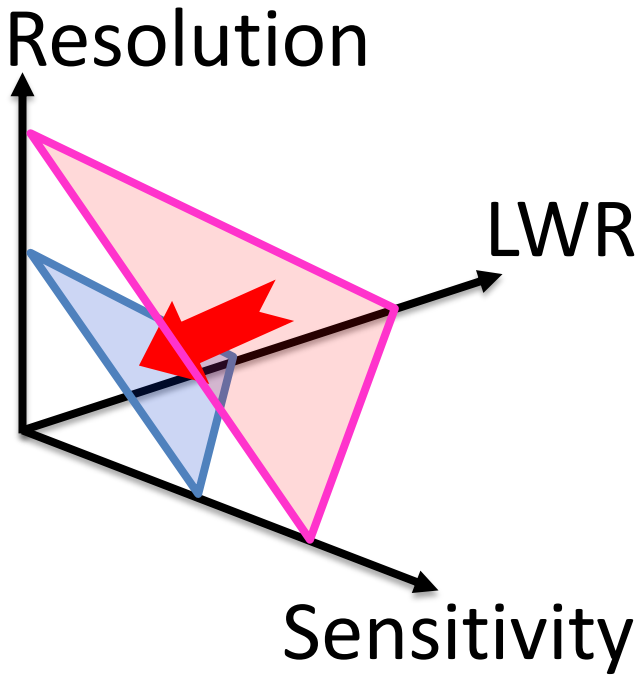
# Issue of EUV Resist

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**EUVL Specific issue**
**Outgassing**

- Requirement of resist performance for EUVL:
  - High resolution
  - Low LWR
  - Fast sensitivity
  - <u>Low outgassing</u>

# Objective of This Work

- <u>What is the main contributor of outgassing species to contamination?</u>
  - Decomposed PAG
    - Y. Kikuchi et. ai.,
    - I. Pollentier et. al., Proc. SPIE., 7972 (2011)
    - I. Takagi et. al., J. Photopolym. Sci. Technol., 26 (2013), 673.

- <u>Impact of PAG structure on outgassing/contamination</u>
  - PAG blended system: cation size
  - PAG bound system: anion bound and cation bound

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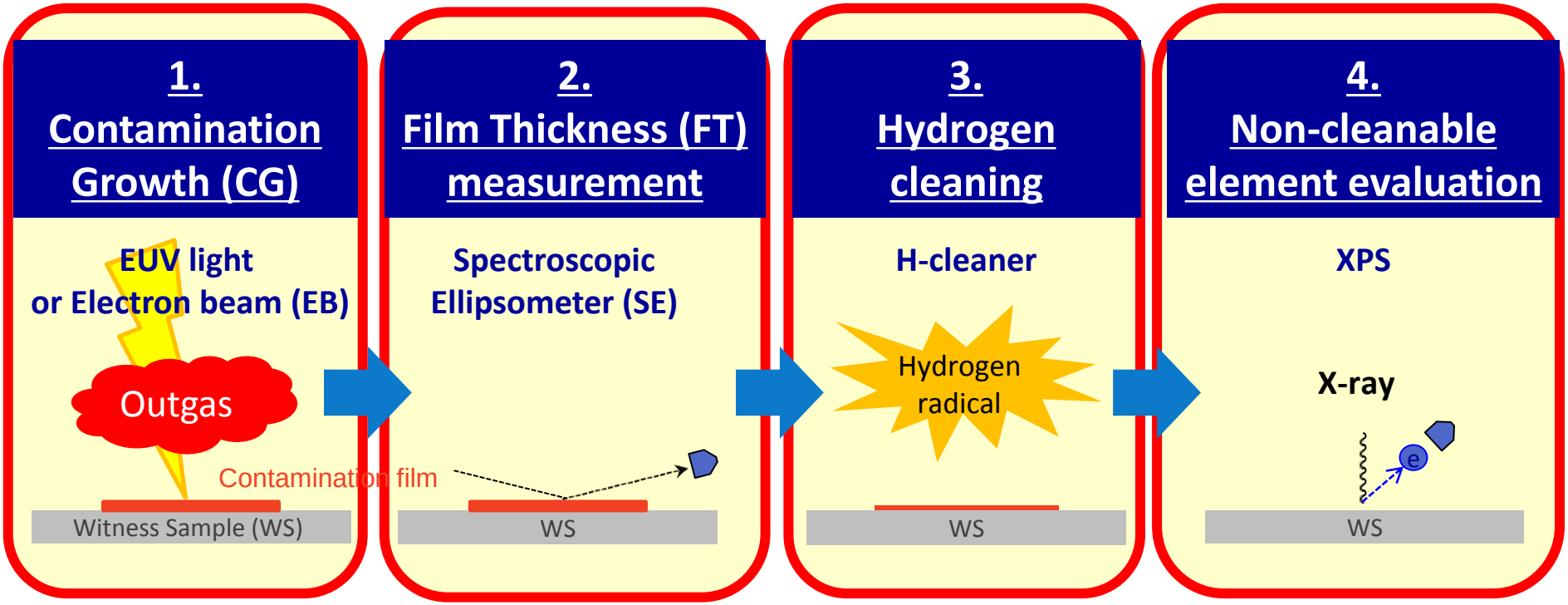
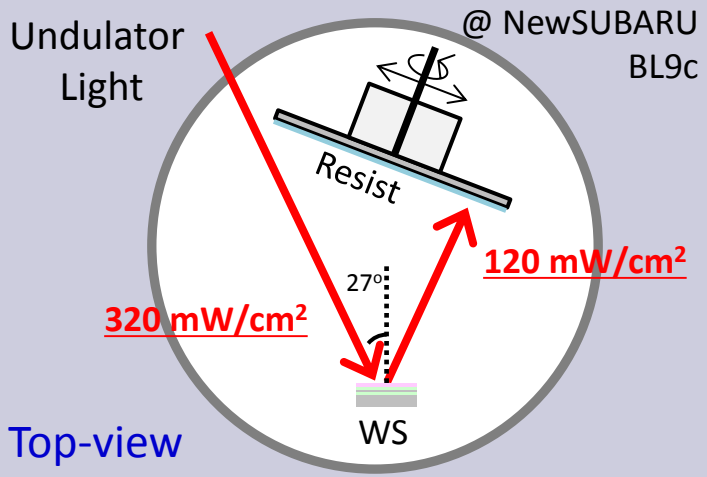
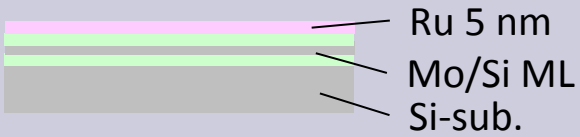
# Process Flow of Outgassing Test

- EUV resists must pass outgassing tests before being allowed exposure in the EUV HVM scanner.
- This is because outgassing components (cleanable and non-cleanable) contaminate the optical system.

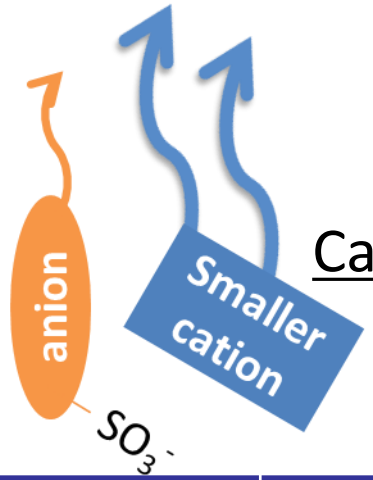


# Outgas Evaluation Tool and Condition

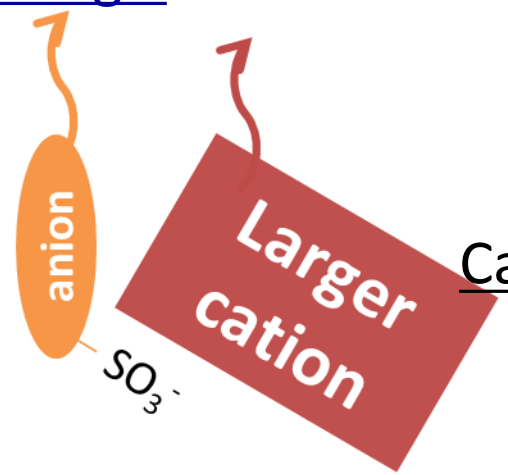
| | High Power EUV Resist outgas Contamination analysis tool (HERC) |
|---|---|
| Tool geometry |  |
| Vacuum conditions | Base: 3~4x10-6 Pa<br>Exposure: 1~2x10-5 Pa |
| Dose | E0 x 2.5 |
| Resist thickness | 60nm |
| Witness Sample (WS) |  |

# Characterization for PAG Cation Size

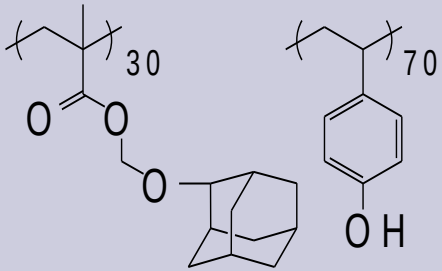
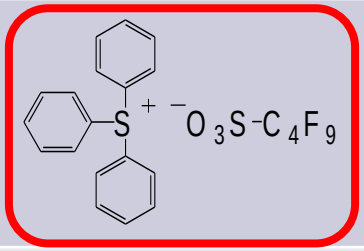
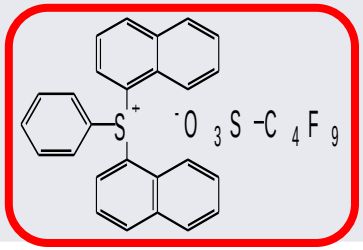
- Large PAG cation → Low outgassing ?




Cation size: Smaller

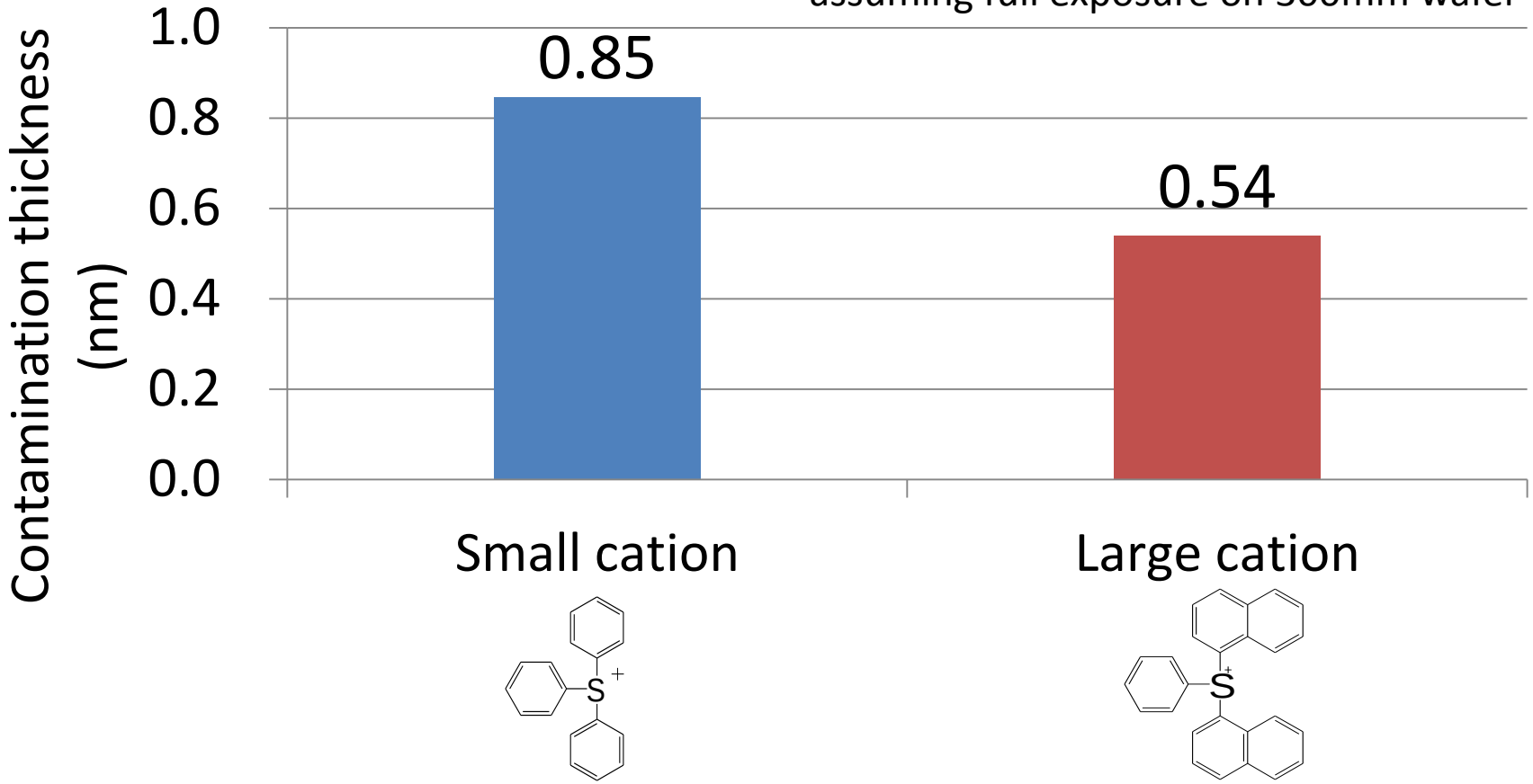



Cation size: Larger

| Blended / Bound | Cation size | Polymer | PAG (equimolar) | E0 (mJ/cm$^2$) |
|---|---|---|---|---|
| Blend | Small |  |  | 2.31 |
| | Large | |  | 3.78 |

# Cleanable Contamination Results: PAG Cation Size

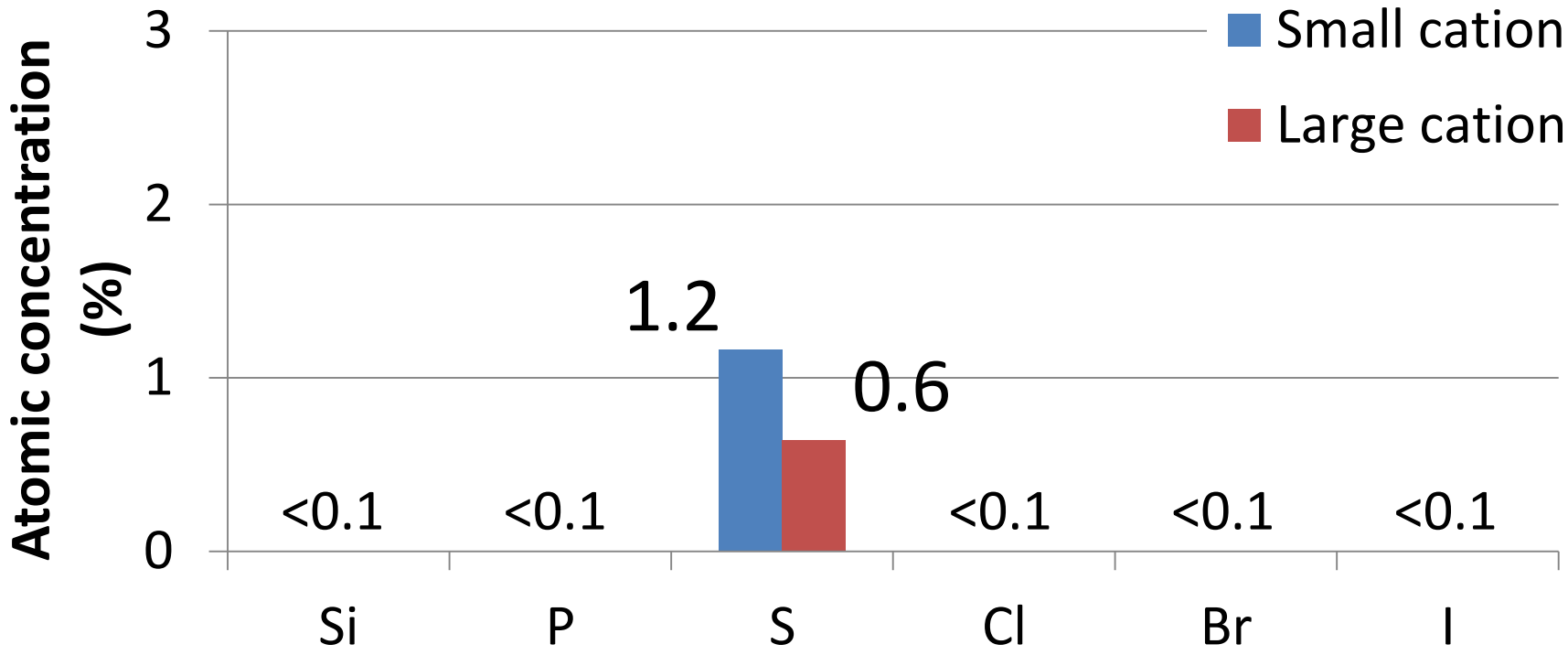
*Calculated contamination thickness: assuming full exposure on 300mm wafer




- Low contamination level is confirmed with large PAG cation.
- Results suggests resist outgas dependence on PAG cation size.

# Non-cleanable Elements: PAG Cation Size

Exposed area




- Regardless of cation size, non-cleanable elements were found to be sulfur (S).
- Cleanable contamination level and S concentration found to have a similar trend.

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- Introduction and Objective
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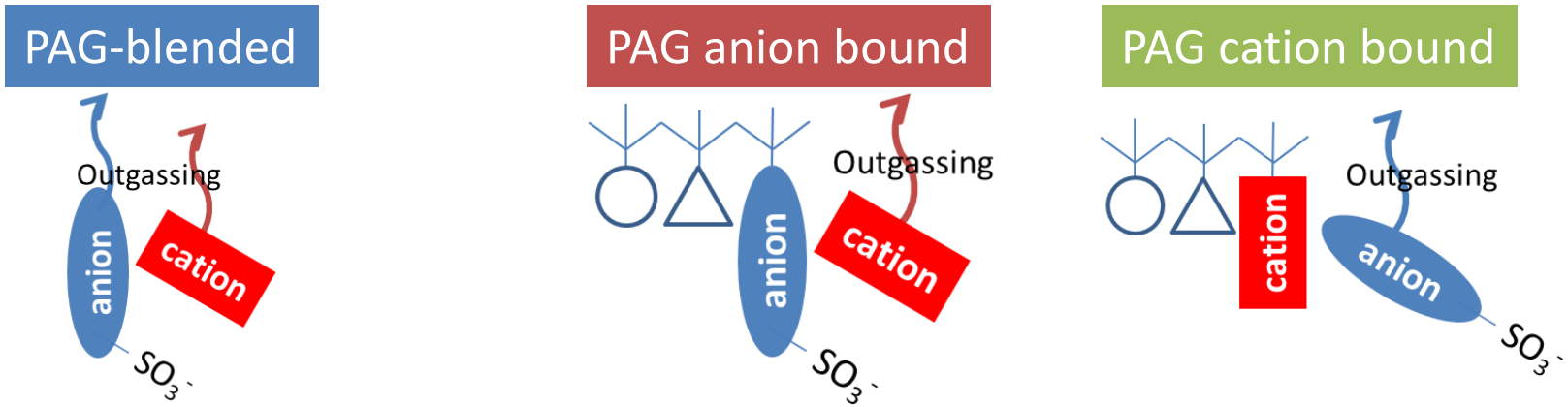
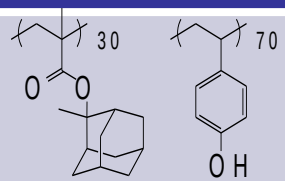
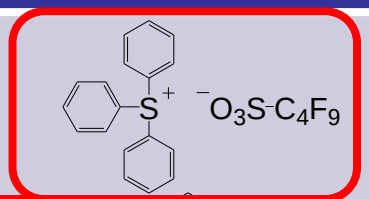
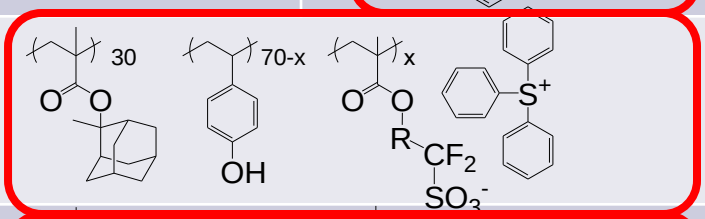
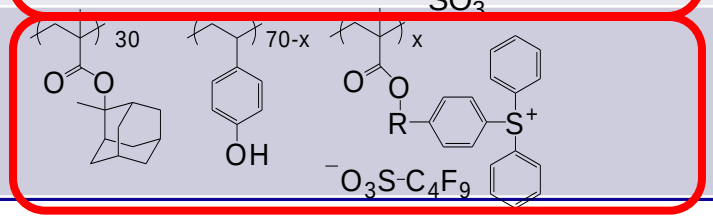
# Characterization for PAG-bound System

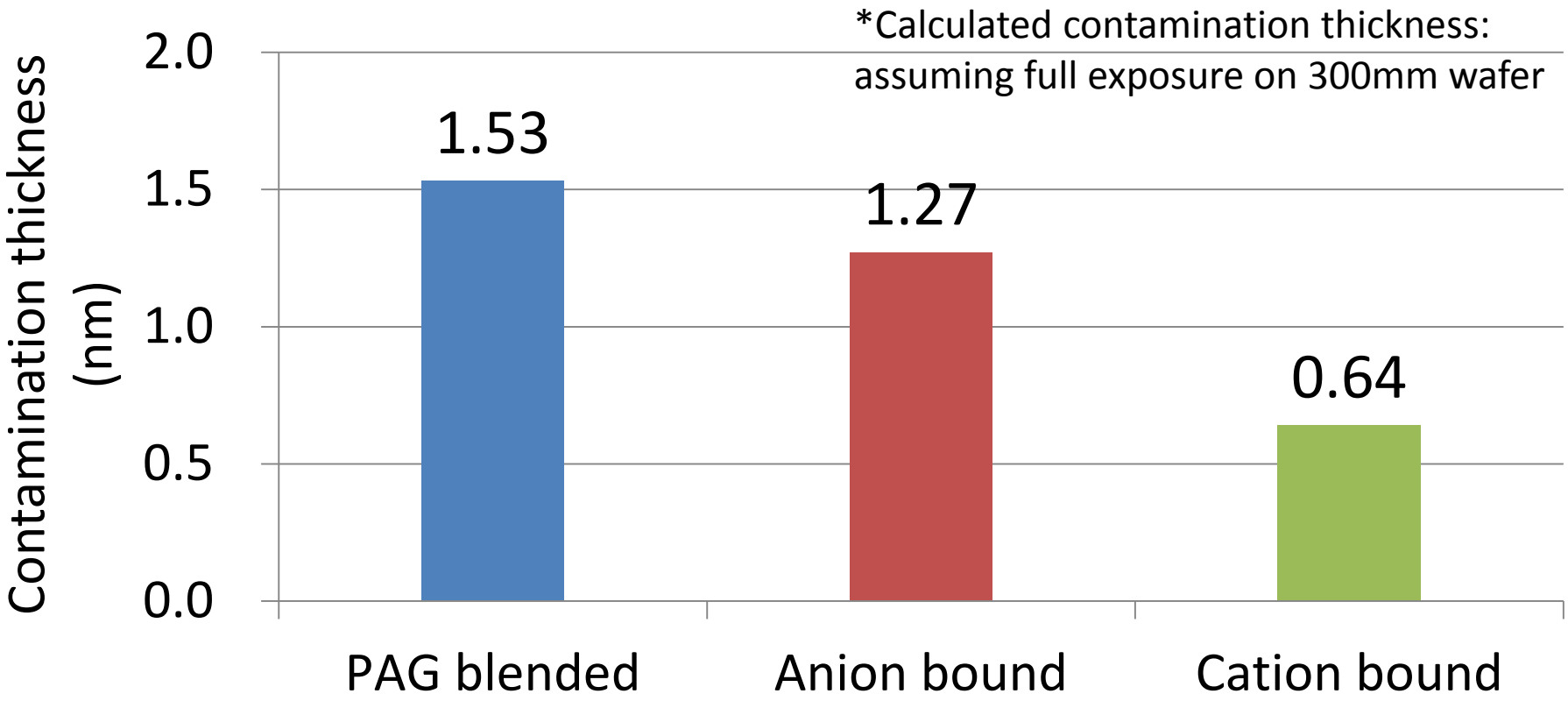
- PAG-bound system → Low outgassing ?




| Blended / Bound | Sample Concept | Polymer | PAG* (equimolar) | E0 (mJ/cm²) |
|---|---|---|---|---|
| Blended | PAG blended |  |  | 3.28 |
| Bound | Anion bound |  | | 3.29 |
| | Cation bound |  | | 4.28 |

*Mw of PAG is similar

# Cleanable contamination results: PAG bound system




- Comparison of cleanable contamination:

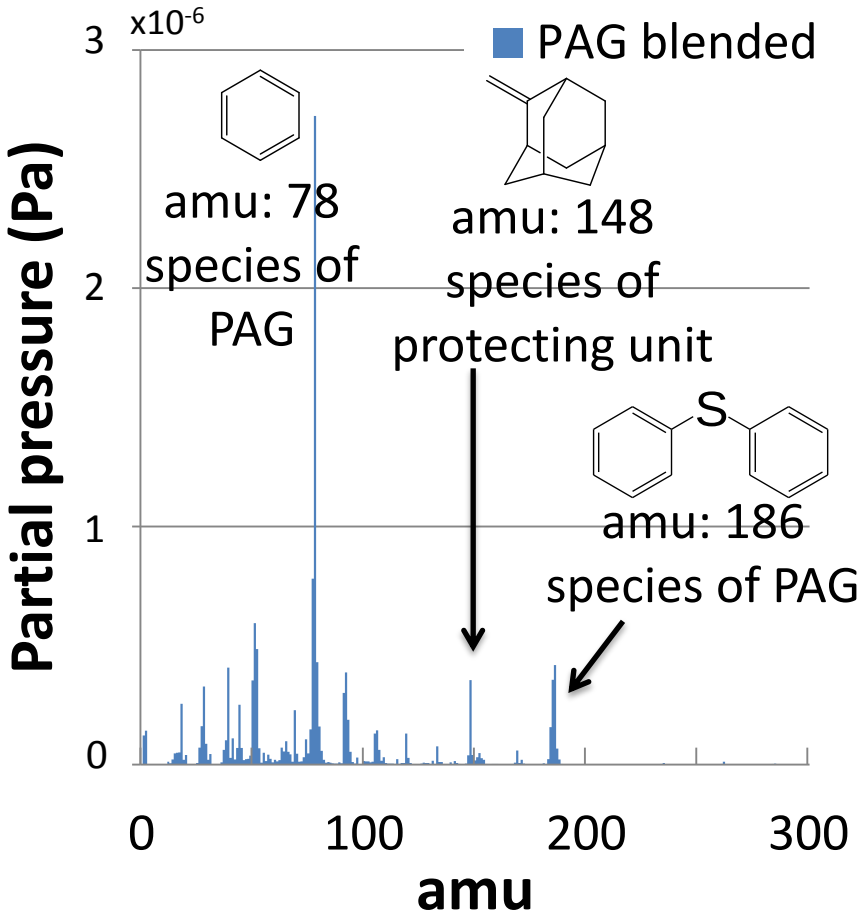
  **PAG blended > Anion bound > Cation bound**

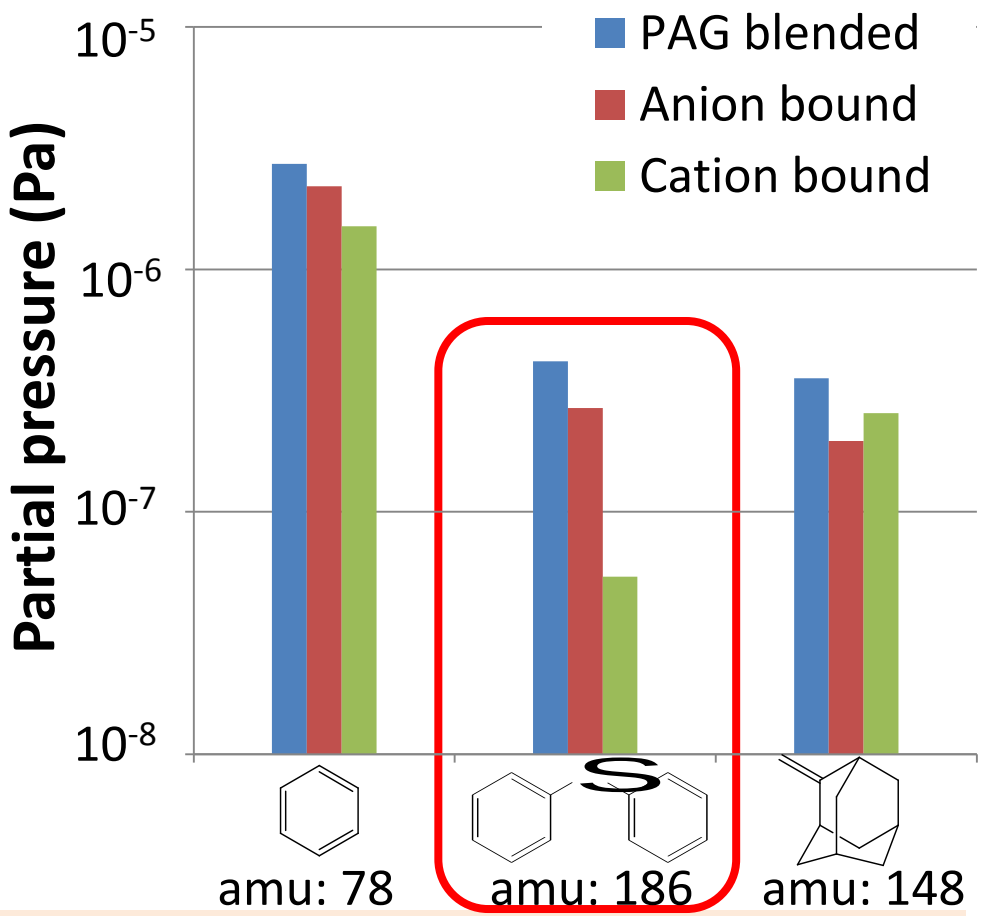
- How about amount of outgas species during exposure?

  →Residual gas analysis(RGA)

# PAG bound System: RGA Results

## Outgassing amount for each PAG system

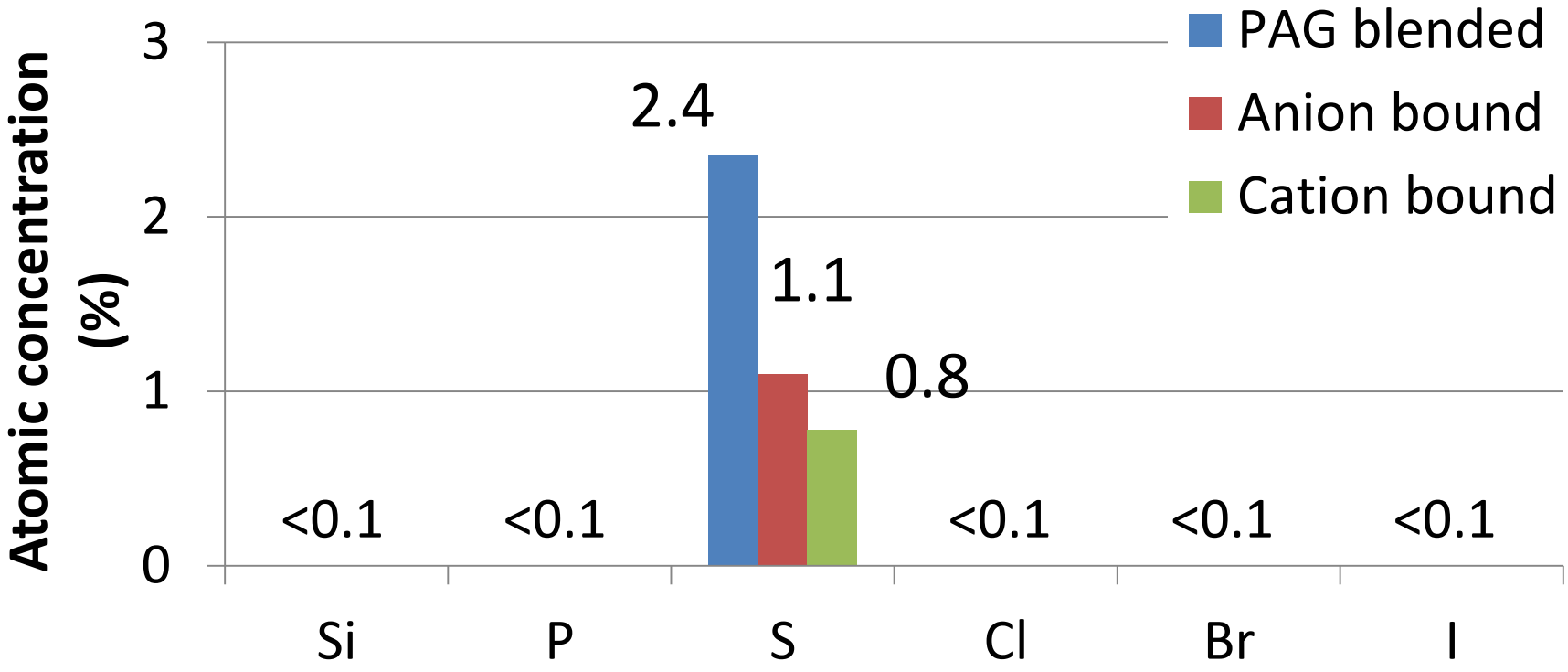



- No significant difference was found in the released de-protected units.
- For di-phenyl sulfide from PAG, cation bound had low total outgassing compared to both of PAG blended and anion bound.

# Non-cleanable elements: PAG bound System

Exposed area

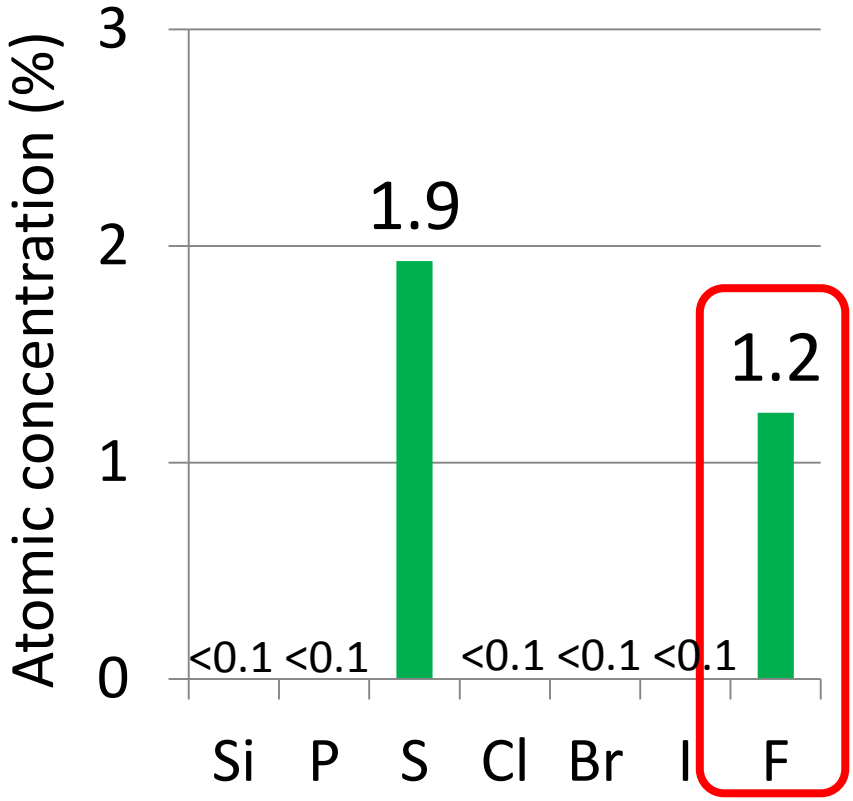



- Non-cleanable elements are S in both blended and bound types.
- S concentration shows a similar trend as cleanable contamination.

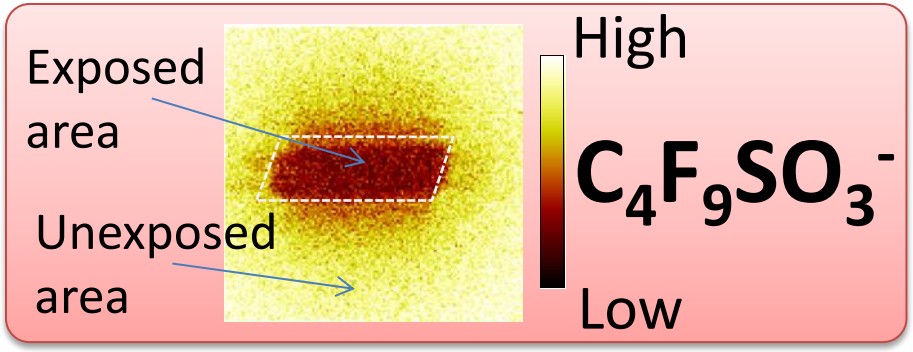
**PAG blended > Anion bound > Cation bound**

# Non-cleanable Contamination on Unexposed Area[1]

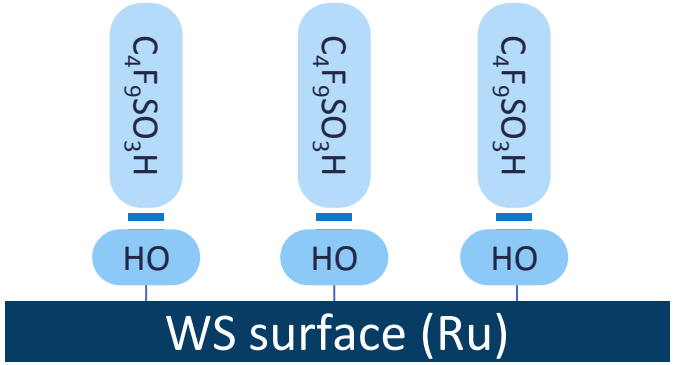
Unexposed area




## TOF-SIMS 2D Scan on WS



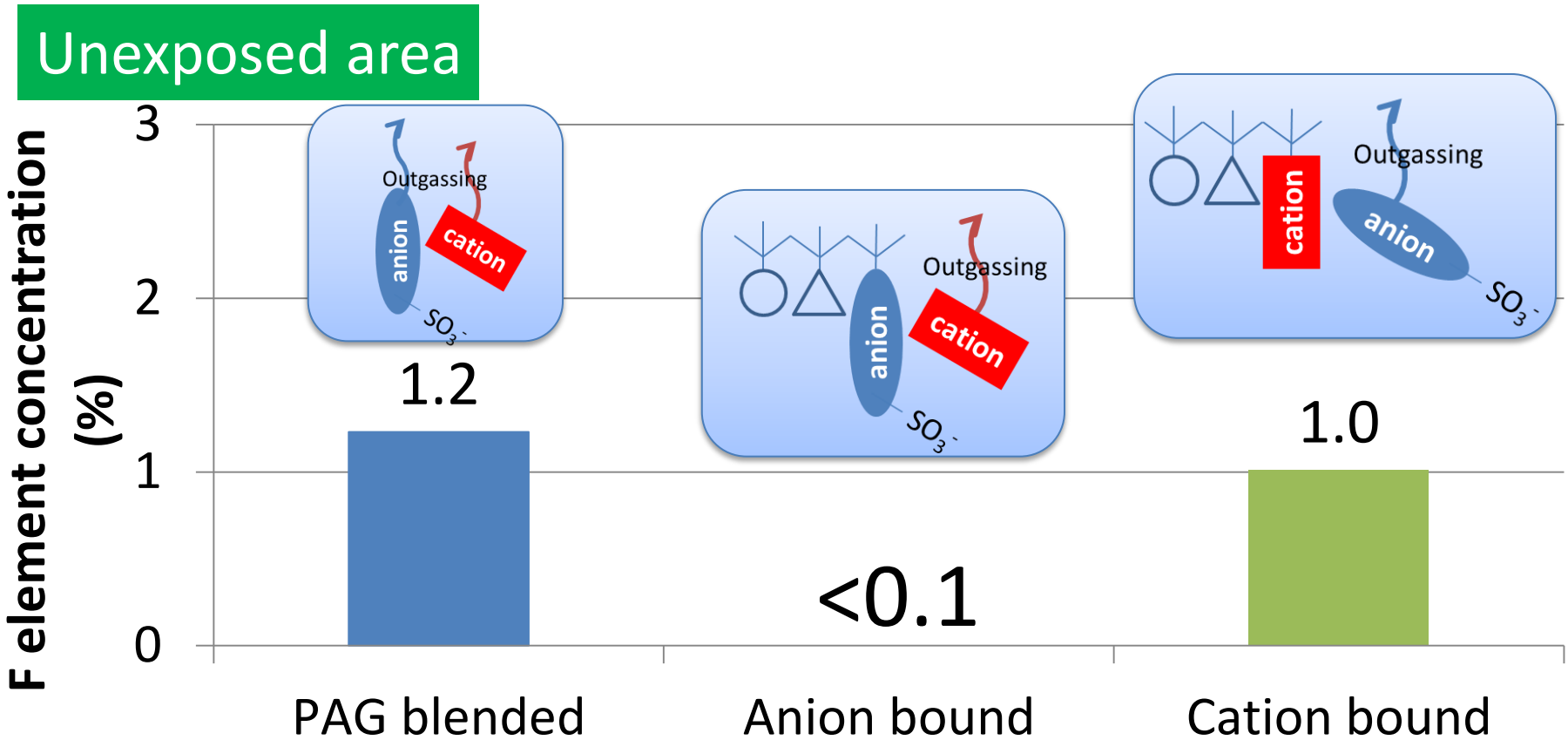

## Model of anion contamination




- From our previous work, the presence of fluorine contamination originated from PAG anion was detected only on unexposed area.
- It is hard to remove anion contaminants due to strong bonding characteristic to the hydrophilic surface of the WS.

[1] T. Takahashi et. al., Proc. SPIE, 8322 (2012)

# Fluorine Contamination of PAG bound System




- F contamination on unexposed area is not detected with anion bound system.
- Anion bound system is useful in reducing the non-cleanable fluorine contamination on unexposed area.

# Summary

- Impact of PAG structure on outgassing and contamination
  - PAG blended system: Cation size
    - Larger cation is lesser cleanable and non-cleanable (sulfur) contamination.
  - PAG bound system: Anion bound and Cation bound
    - Cleanable / Non-cleanable (Sulfur) @ exposed area:

      PAG blended > Anion bound > Cation bound
    - Non-cleanable (Fluorine) @ unexposed area:

      PAG blended ~ Cation bound >> Anion bound

- To reduce outgassing, the material design for PAG cation structure is essential.

# Acknowledgment

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*Thank you for your kind attention!*

***END***